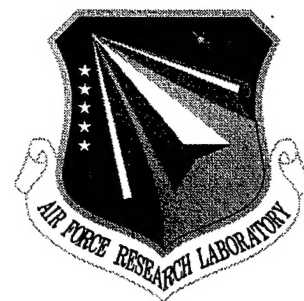


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September 1998



METAL-ORGANIC CHEMICAL VAPOR EPITAXY OF GaN ON Si(111) FOR OPTOELECTRONIC APPLICATIONS

**Research Foundation of SUNY
University at Albany**

A. Kaloyeros, S. Endisch, and A. Topol

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| 13. ABSTRACT (Maximum 200 words) Low temperature growth of gallium nitride on silicon via vapor phase epitaxy was investigated. The use of different nitrogen and gallium sources was explored. The gallium nitride deposition process was optimized by varying surface preparation, seed and buffer layer growth, and annealing conditions. Films were extensively characterized via X-ray diffraction, Rutherford backscatter, atomic force microscopy, X-ray photoemission spectroscopy, and Auger electron spectroscopy. Optimized growth rates of 60-120 A/min were achieved at 0.8 torr pressure, with 1:1 gallium to nitride ratio to within 0.1 %. Films were hexagonal and polycrystalline with 3 nitride bi-layer buffers, with annealing, allowed stoichiometric gallium nitride growth of up to 6000 A, but the temperatures used were not high enough to deposit epitaxial gallium nitride. | | | | |
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Introduction

The focus of our activities has been the growth of epitaxial GaN/Si. The work has focused on demonstrating feasibility of low-temperature VPE processes for high growth rate of pure and stoichiometric GaN films. The development of the process evolved as follows:

- 1) Testing and screening of potential chemical sources for GaN.
- 2) Initial optimization of the process with GaI₃
 - variations in the process parameters
(wafer temperature, sublimation source temperature, process pressure, carrier gas flow, deposition time, and reactant gas flow)
 - measurements of the quality of deposited film
(reproducibility, stoichiometry, growth rate, contamination level).
- 3) Final optimization of the GaN deposition (contamination level and crystallinity)
 - determination of the influence of ex-situ and in-situ preparations of the silicon surface on the GaN film characteristics.
 - determination of the influence of the in-situ annealing on the GaN film characteristics.
- 4) Identification of the appropriate seed layer (improved crystallinity of the GaN film)
 - growth of InN buffer layer
 - growth of AlN buffer layer
- 5) Characterization of the GaN/AlN bi-layer.

Film characteristics were measured by the following analytical techniques:

- X-ray Diffraction (XRD) - crystallinity of the film,
- Rutherford Back Scattering (RBS) - stoichiometry of the films, contamination levels,
- Atomic Force Microscopy (AFM) - film morphology and its roughness,
- X-ray Photoemission Spectroscopy (XPS) - stoichiometry of the films, contamination levels
- Auger Electron Spectroscopy (AES) - stoichiometry of the films, contamination levels

1) Testing and screening of potential chemical sources for GaN.

In terms of the chemical synthesis, the strategy was to select a Ga compound in which the dissociation energy of the primary bonds is relatively low and recombination can be interrupted by the presence of the nitrogen. Two general approaches were proposed for development of the precursor for GaN deposition, one which relies primarily on inorganic chemistry, the other on organometallic chemistry.

During this research period, work was focused on the inorganic route. The candidate chosen was gallium iodide, GaI_3 . This compound is promising since there are precedents for low temperature decomposition of other iodide chemistries such as TiI_4 , through a reaction with NH_3 to generate pure TiN . While the chemistry of the Ga system is not exactly analogous to that of the Ti system, the TiN work gave a clear indication of the ability of iodides to undergo dissociation and recombination reactions at temperatures considerably lower than the chloride compounds (e.g. TiCl_4).

2) Initial optimization of the process with GaI_3

Accordingly, the process development work focused on the growth of GaN/Si using GaI_3 as a Ga source and NH_3 as a nitrogen source. More than 30 GaN test runs were performed to establish a process baseline and determine associated film properties: stoichiometry, purity, and reproducibility. The following process parameter window was investigated:

| | |
|---|-----------------|
| Wafer temperature: | 450 - 550 °C |
| Source temperature: | 150 - 230 °C |
| Process pressure: | 0.2 - 1.5 Torr |
| Reactant gas flow (NH_3): | 200 - 1000 sccm |
| Reactant gas flow (H_2): | 0 - 300 sccm |
| Carrier gas flow (He or H_2): | 10 - 500 sccm |
| Deposition time: | 2 - 15 min. |

Figures 1-3 show that the average growth rate increased with increased source temperature, substrate temperature, and carrier gas flow. Variation in chamber pressure showed that the highest growth rate was achieved at 0.8Torr. Typical growth rates were in the range of 60 - 120 Å/min. Figures 1 - 3 illustrate the discussed trends.

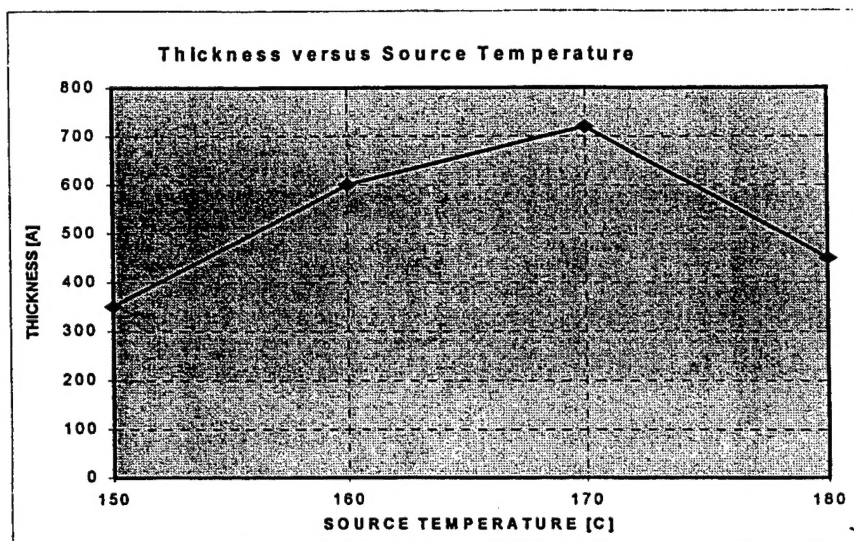


Fig. 1 Thickness vs Source Temperature

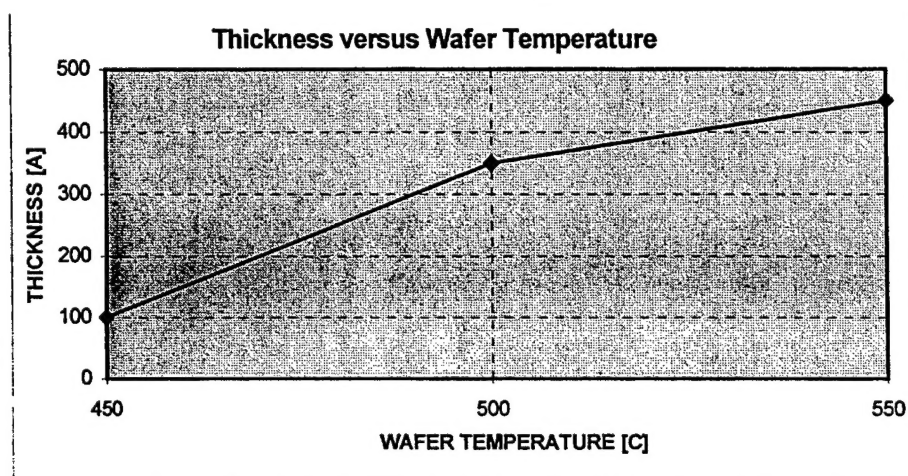


Fig. 2 Thickness vs Wafer Temperature

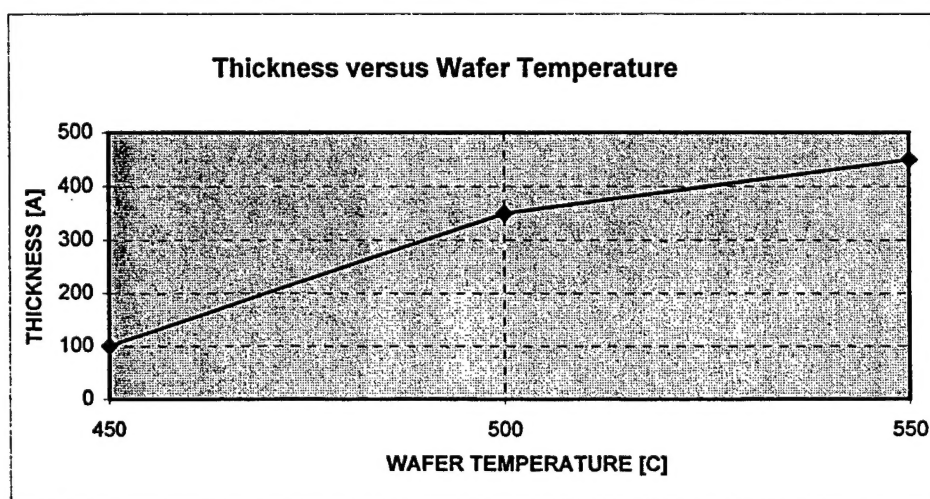


Fig. 3 Thickness vs Wafer Temperature

The desirable film stoichiometry was achieved. The Ga to N ratio is $1 \pm 0.1\%$, as measured by RBS (Figure 4). This is a significant milestone, given the fact that the process temperature was in the range 500-550°C, which is significantly lower than the temperature (>1000°C) used in conventional MOCVD of GaN. Incomplete precursor decomposition can result in high levels of iodide contamination. Films showed 0.2 - 0.5 at% incorporation of iodide, and less than 0.1at% iodide when processed at a substrate temperature of 500°C and 550°C respectively. This was attributed to the availability of more thermal energy at higher substrate temperatures to ensure a more complete precursor decomposition.

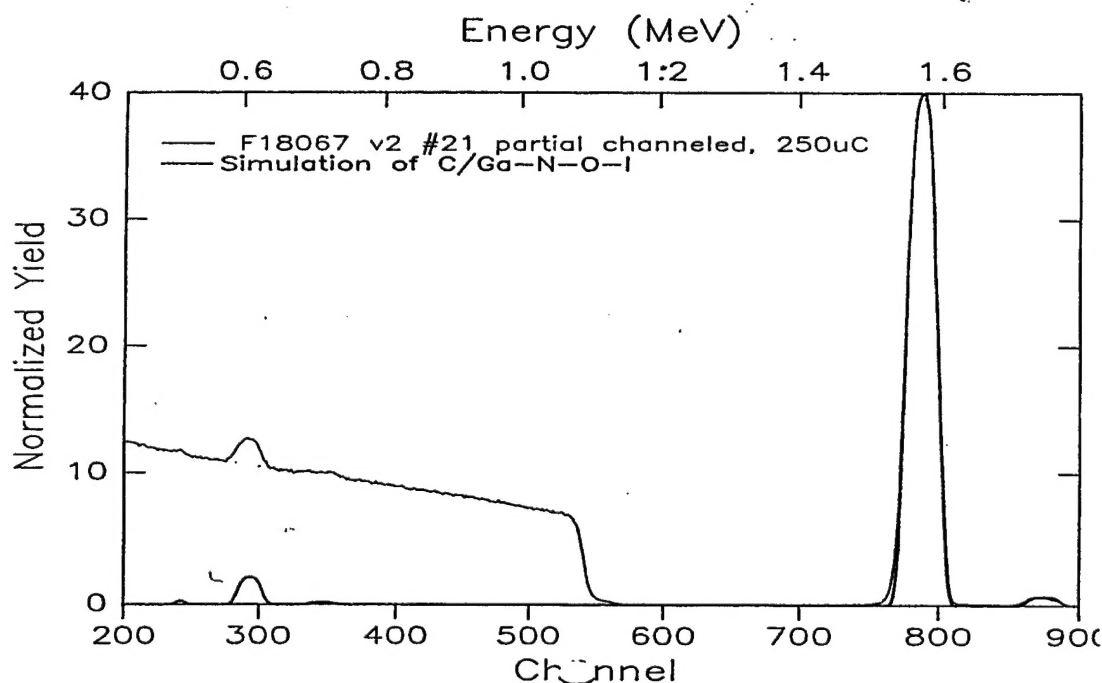


Fig. 4 RBS Results

The levels of oxygen in the film were reduced to 3 at%, with most of the oxygen being present at the film's surface and interface, as measured by XPS (Figure 5). The surface oxygen is due to air exposure leading to oxidation after removal from the CVD reactor, while interface oxygen is due to silicon surface oxide prior to processing. It was clear that in-situ or ex-situ silicon surface pre-deposition cleaning was needed.

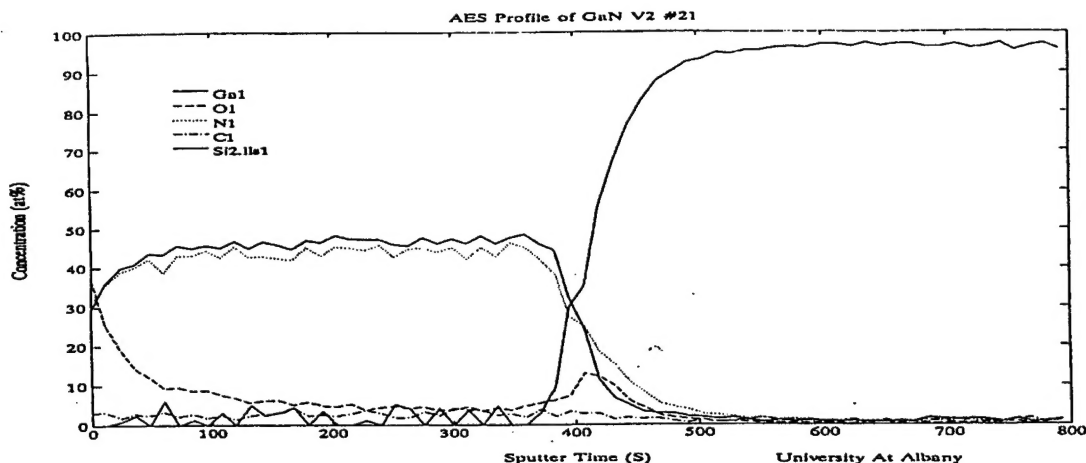


Fig. 5 XPS Results

3) Final optimization of the GaN deposition

3.1 *Determination of the influence of ex-situ and in-situ preparations of the silicon surface on the GaN film characteristics.*

For epitaxial growth of GaN on Si it is essential to start with a clean, oxygen-free silicon surface, therefore different cleaning techniques have been investigated. The Si substrates were rinsed in Acetone, Ethanol and DI water and then outgassed in the load lock prior to their introduction to the deposition chamber. In addition we studied the following ex-situ and in-situ cleaning techniques:

- *sample #45
5 min etch in 10% buffered HF
- *sample #46
5 min etch in 10% buffered HF
10 min in-situ H₂ plasma clean (50W, 0.4torr chamber pressure)
- *sample #49
5 min etch in 10 % buffered HF
20 min annealing at 700°C

All samples were grown under similar process conditions and were analyzed with RBS and AES. The Auger depth profiles reveal that the oxide layer at the GaN/Si interface has been successfully removed for samples #46 (Figure 6) and #49 (Figure 7). XPS data also shows that the oxygen level has been reduced to 1 - 2at% throughout the GaN layer.

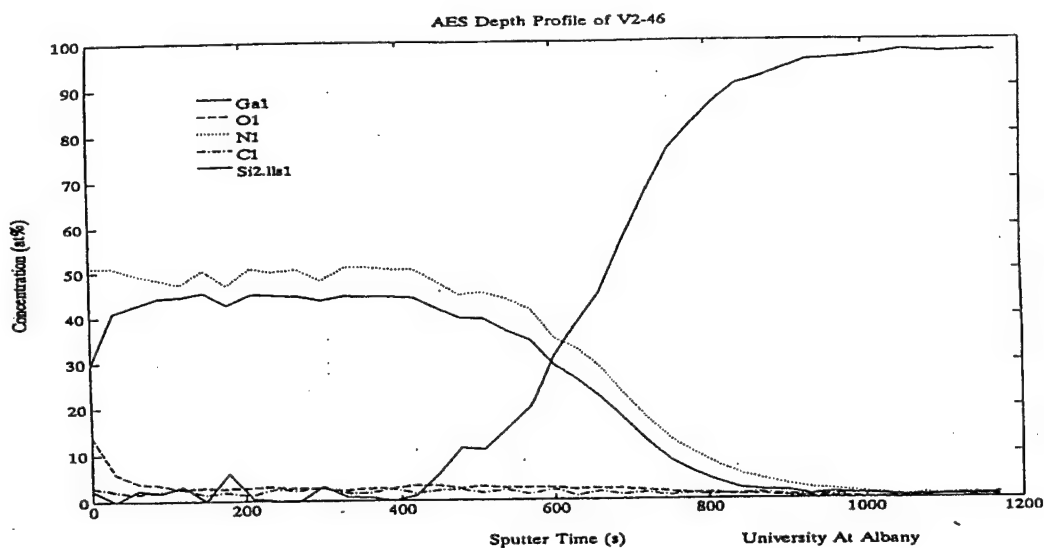


Fig. 6 Auger for Sample 46

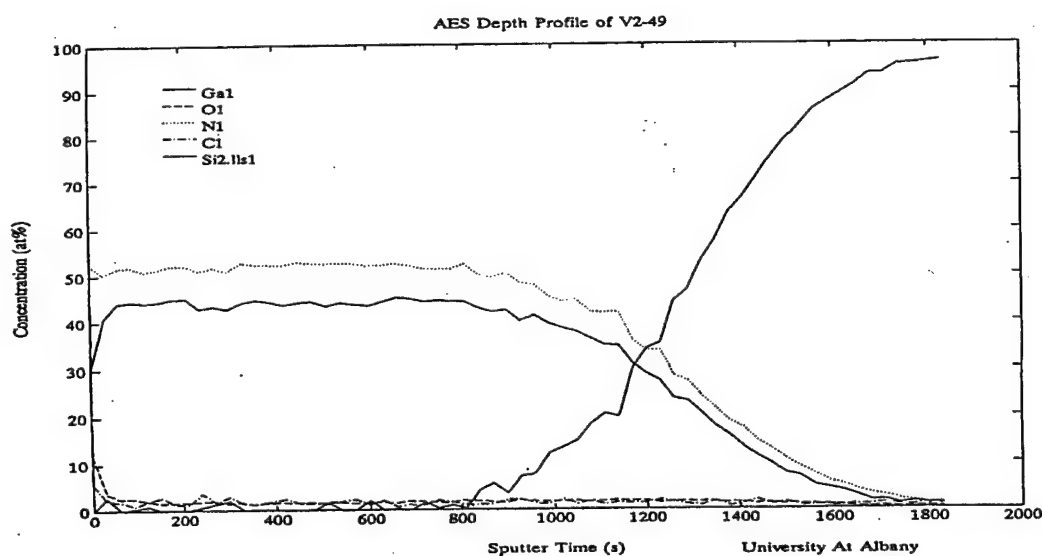


Fig.7 Auger for Sample 49

3.2 Crystallinity and morphology of the deposited films.

The XRD results show that the investigated films have hexagonal crystal structure. This is expected as the cubic structure of GaN is metastable. The films were polycrystalline and most of them exhibited preferred orientation in the (002) direction. It can be seen that the chemical preclean (acetone, ethanol, DI water, 10% HF) greatly

improves the GaN signal. A further improvement in peak intensity as well as in the linewidth is obtained by an in-situ annealing at 770°C (Figure 8).

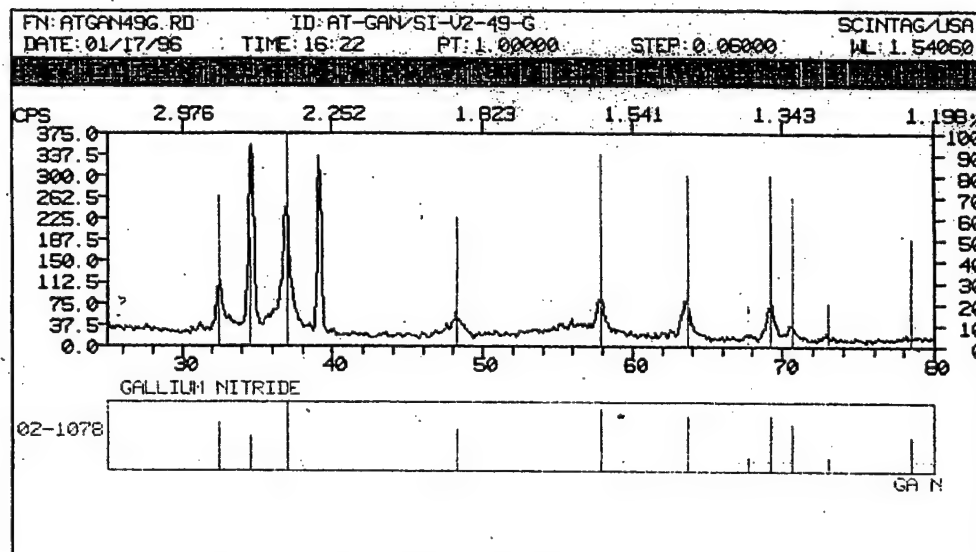


Fig. 8 XRD After Anneal

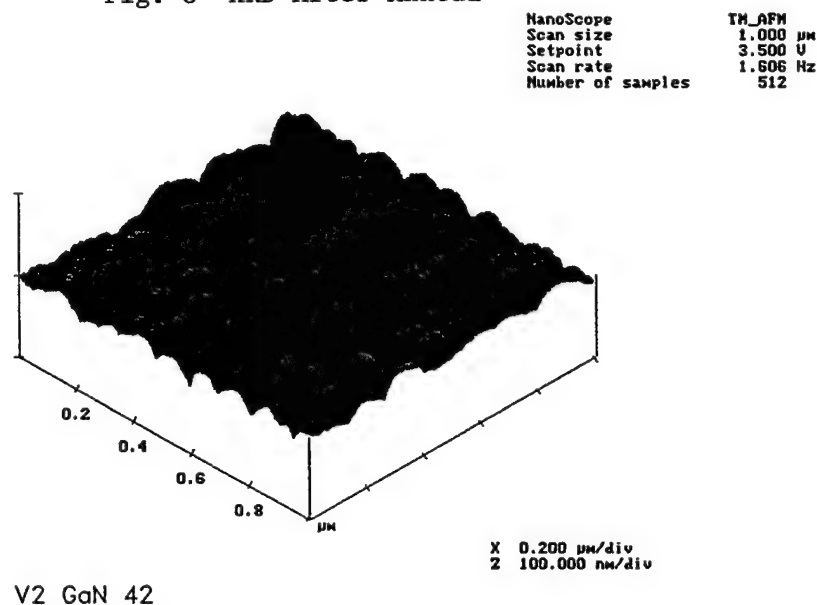


Fig. 9 AFM

AFM measurements were also been performed. The samples were scanned on an area of $1 \times 1 \mu\text{m}^2$. The measured grain size was between 3.5 - 32nm. From these measurements we calculated the roughness of the samples to be between 2 - 8nm (as shown above in Figure 9).

4) Identification of the proper seed layer (improved crystallinity of the GaN film)

4.1 *Growth of InN buffer layer*

In order to improve the crystallinity of the grown GaN film, we needed to grow an appropriate buffer layer. We investigated different materials from the III-V group and chose to grow an InN buffer layer for GaN films deposited on Si. We have identified InI_3 as an In precursor chemistry which is compatible with our current Ga precursor. We used the following process parameters to deposit InN/Si :

| | |
|------------------------|-----------------------------|
| Wafer temperature: | 400 - 765 °C |
| In source temperature: | 30 - 210 °C (melting point) |
| Process pressure: | 0.5 - 1.5 Torr |
| Carrier gas flow (He): | 25 - 50 sccm |
| RF plasma power: | 0 - 200 W. |

The thermal process showed no deposition of InN according to RBS analysis. The plasma assisted process lead to minimal deposition of InN. Poor thermal stability of InN therefore requires an unacceptably high deposition temperature ($\sim 1000^\circ\text{C}$ - typical problem for CVD of InN).

4.2 *Growth of AlN buffer layer*

AlN was another candidate discussed as a seed layer for GaN films. The precursor used to deposit AlN in our studies was DMAH (dimethylaluminumhydride). The process parameters used to deposit this film on Si(100) are listed below:

| | |
|--------------------------------------|----------------|
| Wafer temperature: | 400 - 550 °C |
| In source temperature: | 25 °C |
| Process pressure: | 1.2 - 1.5 Torr |
| Reactant gas flow (N_2): | 200 - 900 sccm |
| Reactant gas flow (NH_3): | 100 - 230 sccm |
| DMAH flow: | 0.5 - 5.0 sccm |

RBS measurements show a near stoichiometric ratio of N to Al as 1.2 (Figure 10) with 4 at% of oxygen, less than 1at% of iodide, and carbon below the detection limit of XPS (Figure 11). AlN films were polycrystalline showing the hexagonal crystal structure (measured by XRD) with roughness $\sim 1.1\text{nm}$ measured by AFM (Figure 12).

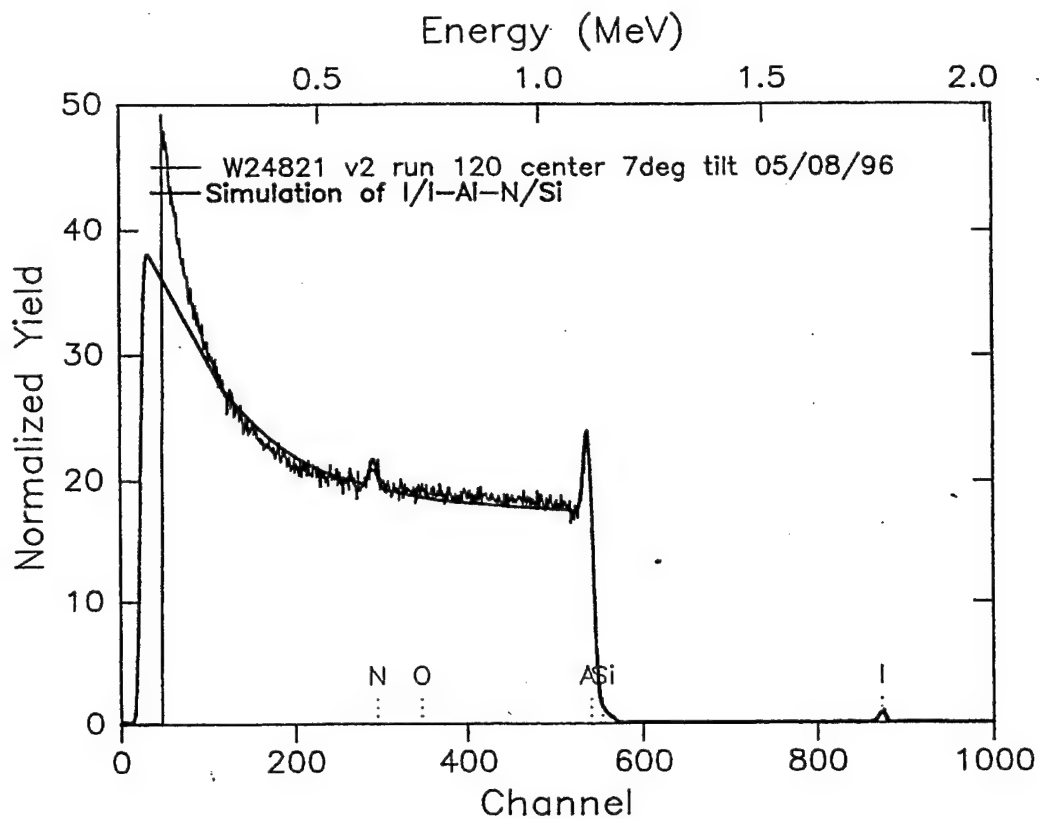


Fig. 10 AlN RBS Results

ESCA PROFILE 5/9/96 START=1, END=26, NTH=1
FILE: V2_119_3 V2 #119 (Al)

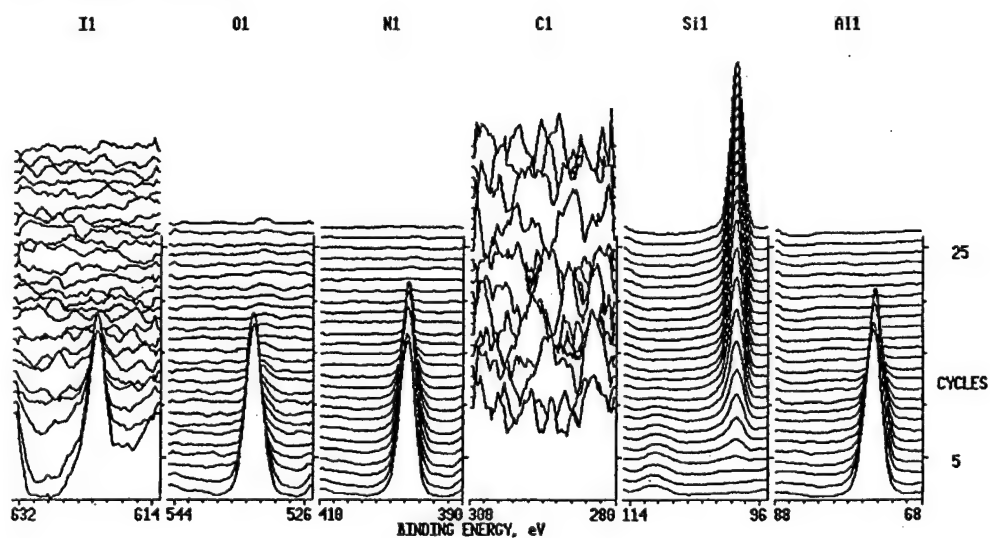


Fig. 11 AlN XPS Results

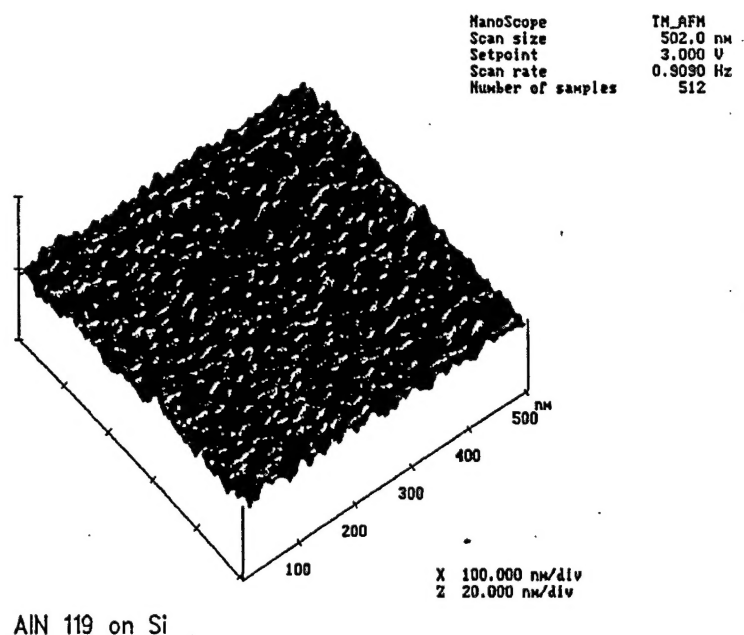


Fig. 12 AlN AFM Results

5) Characterization of the GaN/AlN BI-layer.

Once a reproducible deposition process was established for AlN, we progressed to bi-layers. The parameters of the individually optimized process windows for AlN and GaN used in the deposition of the bi-layer on Si are listed below:

| | AlN | GaN |
|---------------------------------------|---------------------------|-------------------------------|
| Wafer temperature: | 450 °C | 500 °C |
| In source temperature: | 26 °C | 160 °C (cooled after melting) |
| Process pressure: | 1.2 torr | 0.8 torr |
| Reactant gas flow : | 700 sccm / N ₂ | 200 sccm /H ₂ |
| Reactant gas flow (NH ₃): | 100 sccm | 200 sccm |
| Carrier gas flow (He): | | 25 sccm |
| deposition time: | 5-15min | 10min |

Resulting films were measured by RBS and showed a Ga to N ratio of 1 indicating that the film was stoichiometric (Figure 13). Contamination levels measured in these films by XPS shows 3at% of oxygen and less then 1at% of iodide in GaN layer.

The 250Å of AlN seed layer (5 min deposition time) resulted in the subsequent thickness of 860Å of GaN (run #124) as measured by RBS. On the other hand, 1360Å of AlN seed layer (15 min deposition time) resulted in 1400Å of GaN (run #123). This results points to a possibility of different nucleation / growth mode for GaN when deposited on top of the AlN layers with varying thickness.

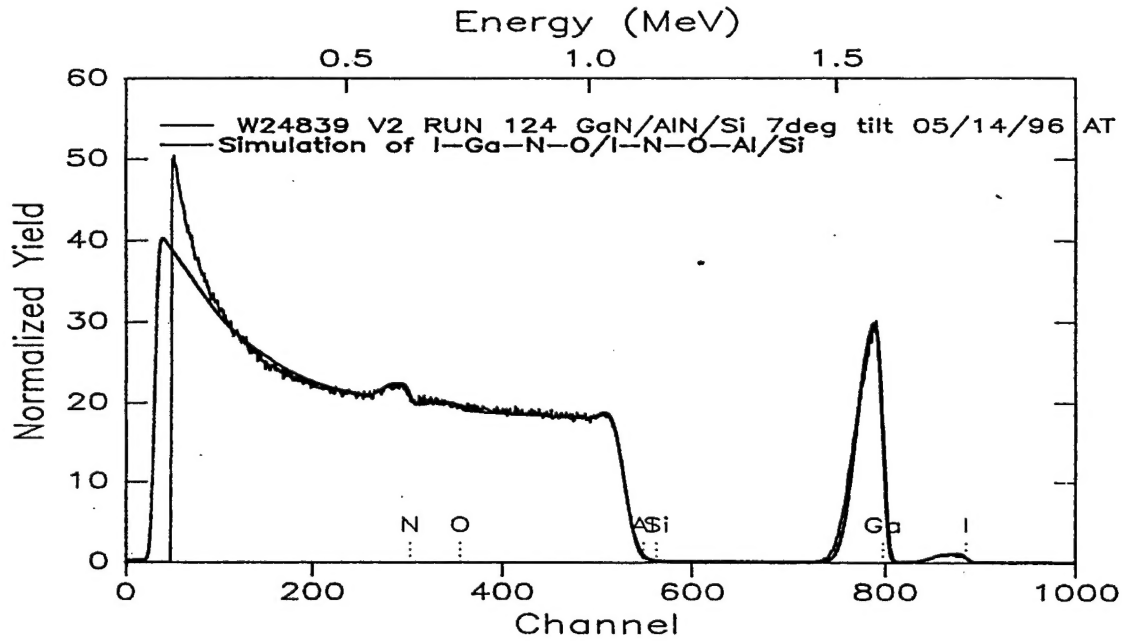


Fig. 13 GaN/AlN RBS Results

Figure 14 shows XRD spectra of three GaN/AlN bi-layers. Sample #123 (as mentioned before) has a thick AlN underlayer of hexagonal crystal structure clearly detectable by XRD. Sample #124 has three times thinner AlN underlayer with twice as thick GaN layer. Therefore it is possible that our XRD set up might not be sensitive enough to pick up signal from the AlN layer. Therefore the time of 10min for AlN deposition was chosen for all other films in order to ensure the accuracy of XRD measurements (this corresponds to ~500Å thick AlN film - which is a thickness often used for AlN buffer layers as cited in many publications on the deposition of epitaxial GaN films). Figure 14 also shows the XRD of sample #125 (substrate temperature 600°C for GaN growth). We can see the GaN grown at higher temperature on the top of AlN buffer layer shows a narrowing of the (002) peak, when compared with films deposited in

the same manner at lower temperature (example #123 and #124), indicating improved crystallinity.

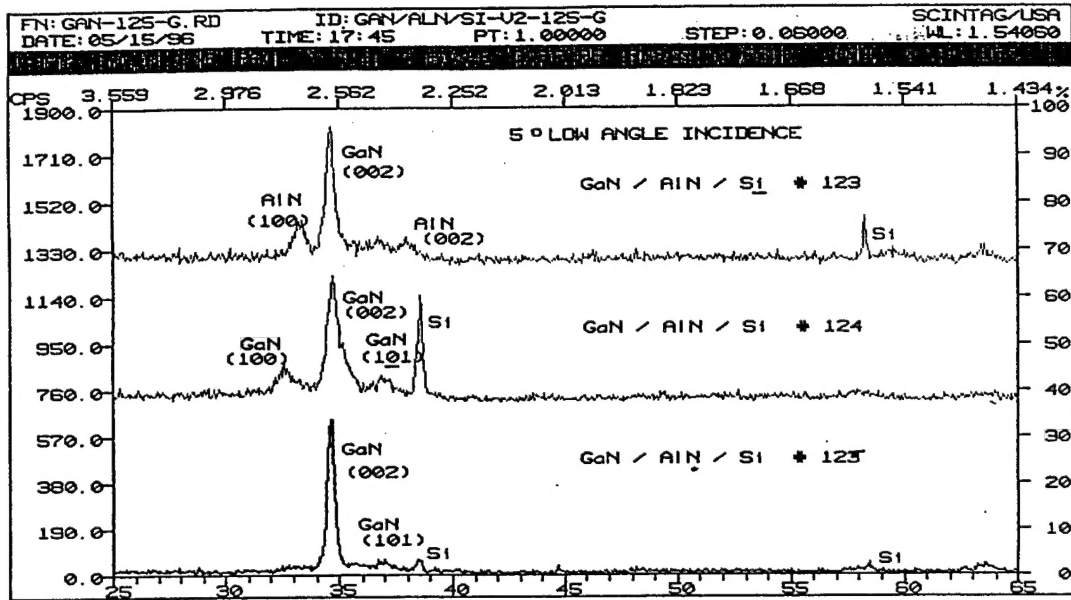


Fig. 14 XRD for Sample 125

Most of the work was focused on achieving the epitaxial GaN/AlN layer on Si. We introduced an annealing step between AlN and GaN deposition (recommended in many publications on GaN epitaxial growth). We performed 13 runs investigating the influence of the annealing temperature (400-700°C for 1 hour) on the orientation of the grown films. After annealing in N_2 , the GaN layers were grown at 550°C with thickness ranging from 600 to 6000Å. XRD measurements show GaN and AlN peaks in the normal and grazing angle scans. The rocking curve measurement (for both AlN and GaN peaks) shows a preferred orientation along the c-axis for samples annealed at 700°C. The measurements also reveal a hexagonal crystal structure for both the AlN and the GaN layers. This texture is not present for samples annealed at temperatures lower than 500°C (see Figure 15).

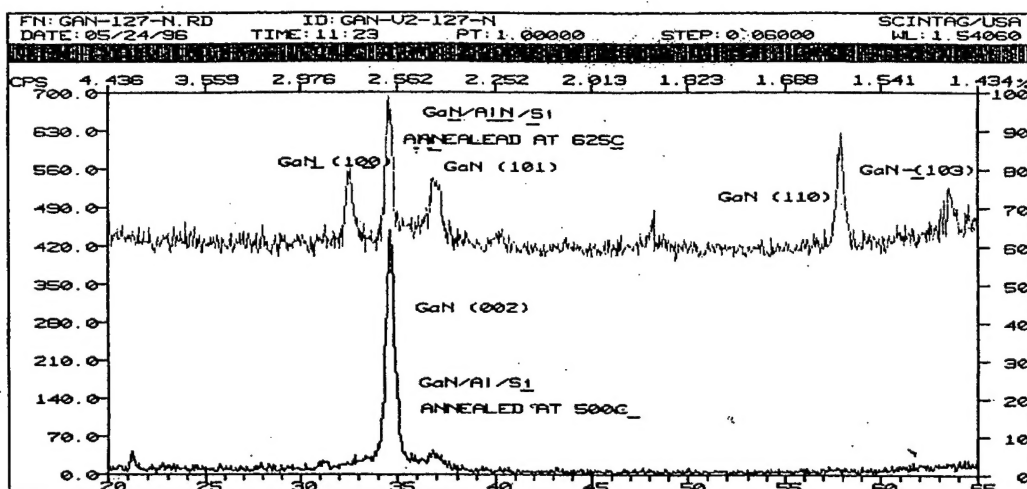


Fig. 15 XRD Anneal Results

Conclusions

Significant milestones were achieved during our studies on the growth of the GaN. We developed a low temperature VPE process to deposit this material. We were able to deposit stoichiometric GaN on the Si. This work was supplemented with buffer layer studies allowing for growth of high quality material (oxygen contamination level below ~3at%, iodide below 1at% and carbon below detection level of XPS).

We investigated the effect of the Si substrate cleaning (prior to the deposition of GaN) on properties and characteristics of GaN film. In addition we studied the influence of annealing steps on the crystallinity and morphology of the deposited materials. Implementation of these findings in our final deposition process (bi-layers) allowed us to demonstrate the feasibility of low-temperature VPE process for the growth of GaN/AlN on Si.

XRD measurements showed hexagonal crystal structure of AlN and GaN layers with preferred orientation along the c-axis. In order to grow an epitaxial GaN high process temperatures are required (~1000°C for CVD, ~800°C for MBE, and ~700°C for PACVD). Since our process was based on deposition in a range of 400 - 765 °C we were not able to deposit an epitaxial GaN.